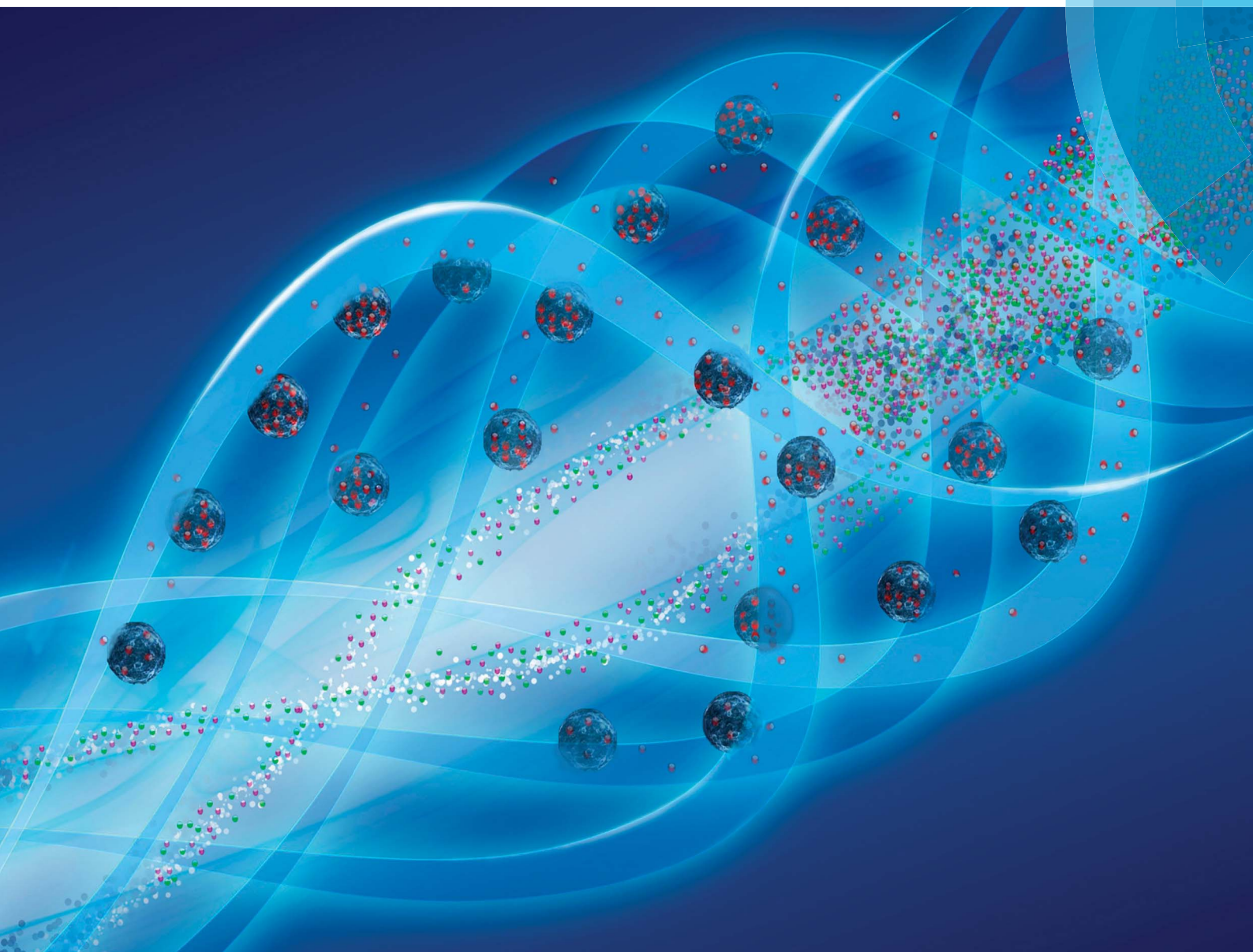


Analytical Methods

rsc.li/methods



ISSN 1759-9679



PAPER

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Cite this: *Anal. Methods*, 2018, 10, 3144

Composite materials based on hybrid mesoporous solids for flow-through determination of ultratrace levels of Cd(II)[†]

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In this work we present a solid phase extraction (SPE) flow-through system coupled to graphite furnace atomic absorption spectrometry (GFAAS) for the determination of Cd(II) at ultratrace levels. The flow system holds a minicolumn which was filled, one at a time, with three different lab-made materials: (a) mesoporous silica functionalized with 3-aminopropyl groups from 3-aminopropyl triethoxysilane (HMS); (b) HMS with a resin, Amberlite IR120; and (c) HMS-Amberlite IR120 and polyvinyl alcohol (PVA). All the solids were characterized by FTIR and SEM. Batch experiments were performed in order to study the optimum adsorption pH, the adsorption kinetics and the maximum adsorption capacity. The materials were compared in terms of their aptitude for the pre-concentration of the analyte under dynamic conditions. Microvolumes of HCl were employed for the release of cadmium and its introduction into the electrothermal atomizer. The operational variables of the flow system were also tested and optimized. A comparison of the figures of merit revealed that HMS-A-PVA was the best option from an analytical point of view: limit of detection = 4.7 ng L⁻¹, limit of quantification = 16 ng L⁻¹, RSD% = 4 ($n = 6$, 100 ng L⁻¹), linear range: from LOQ up to 200 ng L⁻¹ and a lifetime of over 600 cycles with no obstructions to the free movement of fluids, material bleeding or changes in the analytical sensitivity. The proposed method was shown to be tolerant to several ions typically present in natural waters and was successfully applied to the determination of traces of Cd(II) in real samples. A full discussion of the main findings with emphasis on the metal ion/filling interaction is provided.

Received 19th April 2018

Accepted 6th June 2018

DOI: 10.1039/c8ay00879e

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1. Introduction

Cadmium is a persistent pollutant of high toxicity to animals and human beings even at extremely low concentrations and it even acts as a human carcinogen.¹ It is easily accumulated in living organisms and concentrated through the food chain. The appropriate guideline values for cadmium content for drinking water by the WHO² and USEPA³ are 3.0 µg L⁻¹ and 5.0 µg L⁻¹, respectively. Since human activities have increased its use, it is mandatory to develop reliable analytical methodologies able to determine cadmium at trace levels in all kinds of samples.

As reviewed by Płotka-Wasyłka *et al.*,⁴ monitoring of compounds present in complex samples at trace or ultratrace levels usually requires a preliminary step of isolation and/or preconcentration. Solid phase extraction (SPE)^{5,6} can meet

these requisites, becoming of great value for analytical chemists.

Consequently, SPE has been widely used either in batch or in column with the aim of retaining compounds, elements or species on different solid materials, with the elution of the analytes being performed with suitable chemical reagents.⁴⁻⁸ The main features of the preconcentration/elution cycles are quantitative retention and quantitative elution of the analyte, together with a high preconcentration factor.⁴⁻⁹

Minicolumn SPE has proven to be advantageous when properly managed. It allows improving the analytical performance of a given methodology, including the reduction of costs due to high sample throughput, low amounts of reagents, reduction of waste, environmental safety, *etc.*⁴⁻¹² Even though the use of SPE has been improved in the past few years through the development and refinement of new supporting formats and stationary phases (*e.g.* activated carbon, amorphous silica, clays, zeolites, organic chelating resins, ion-imprinting polymers, *etc.*), many of these materials suffer from problems such as low retention capacity, low selectivity, long equilibration times, mechanical and/or thermal instability, *etc.* On this subject, several studies devoted to the design of new supports and new synthetic sorbents have been reported in the literature.⁸⁻¹⁹ For example, resins based on styrene-divinyl benzene

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ay00879e

have been used mostly for removal of contaminants. Approaches involving surface modification, impregnation or grafting have been reported in the literature.^{20–22}

Silica based mesoporous materials synthesized *via* the templating function of surfactant micelles^{4,6,8,19,23} yield an organic–inorganic hybrid with a pre-designed structure. From an analytical point of view hybrid mesoporous silica (HMS) presents good adsorption capacities, high reproducibility of the retention step, large lifetimes, and excellent prospects for specificity,^{19,23,27} the latter being mainly due to its high flexibility for functionalization.^{4–11,19,23–27} Moreover, polymeric composites consisting of HMS and organic polymers represent a new class of materials that exhibit improved performance compared to their isolated components.²⁸ As a result, amino-functionalized porous hybrids and polymer composites have been fully investigated as potential adsorbents of heavy metal cations^{10,11,25,29–36} or organic molecules³⁷ demonstrating the combined advantages of the developed porous framework and the functional groups.^{23–38} Nonetheless, most of the studies in the literature highlight the physical and chemical interaction of the compound under study and the synthesized solid^{12,19,23,24} leaving apart the quantitative release of the retained compound, which is mandatory for analytical purposes.

Finally, there is an important development of SPE sorbents derived from the combination of different compounds since they allow high selectivity, ease of use, simplicity in terms of synthetic procedure, less consumption of organic solvents, and reduction of dangerous waste, all in agreement with the principles of green chemistry.^{4,19–24}

According to this, we present the synthesis of mesoporous silica functionalized with 3-aminopropyl groups, and its combination with two new composite materials, one blended with the resin Amberlite™ IR120 (HMS-A) and the other blended with the same resin and the polymer polyvinyl alcohol (HMS-A-PVA).

The resin blended composite was thought to be a way of obtaining a greater tortuosity of the pathway within the column and thus, to increase the exposure of the analyte to the amino groups of the HMS and, possibly, the number of chelating groups.

Regarding the HMS-A-PVA, it was considered that the incorporation of a water soluble polymer in a proportion that ensures adherence but not complete coverage of the original material (HSM-A) could impose a synergic effect on the chelating properties.

The structure and morphology of the sorbents were characterized by Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis of HMS.

The operational conditions for the adsorption/desorption of Cd(II) were optimized through static and dynamic experiments. These three sorbents were used for the preconcentration of Cd by flow-through minicolumn SPE coupled to GFAAS. The figures of merit of the three approaches were compared to each other and to other alternatives recently reported in the literature, revealing that HMS-A-PVA had the best analytical performance. Finally, the proposed methodology was applied successfully for

cadmium preconcentration in real samples. As far as we know, this is the first time that a blend between a resin and a hybrid mesoporous material modified with PVA has been used for flow-through preconcentration in a minicolumn coupled to GFAAS for the determination of ultratrace levels of Cd(II).

2. Experimental

2.1. Reagents

Standard solutions of Cd(II) were prepared by proper dilution of 1000 g L⁻¹ stock solutions (Merck Darmstadt, Germany) with double deionized water, DDW, (18 MΩ cm⁻¹, MilliQ Water System, Millipore, Bedford, MA, USA). The pH of the solutions was changed through the addition of suitable quantities of HCl or NaOH solutions (Merck) (1 mol L⁻¹).

Tetraethylorthosilicate (TEOS) 98%, cetyl trimethylammonium bromide (CTAB) ($M = 364.46 \text{ g mol}^{-1}$) and 3-aminopropyltriethoxysilane (APTES) from Sigma-Aldrich (Steinheim, Germany) were employed for the synthesis of the organic–inorganic mesoporous solids.

For solid-phase modification the cationic resin Amberlite™ IR120 and polyvinyl alcohol (PVA) polymer powders (Sigma-Aldrich, 99% hydrolysed, $M_{av} = 89\text{--}98\ 000 \text{ g mol}^{-1}$) were used.

All operations were performed in a laminar flow hood. Nalgene glassware (Nalge, Rochester, NY, USA) was washed with a nitric acid solution (50 : 50 HNO₃ : DDW) and rinsed with DDW, ethanol and acetone.

2.2. Apparatus

A pH-meter (Boeco BT-500, Germany) with a glass working electrode and a reference electrode of Ag/AgCl was used for pH measurements. FTIR spectra were collected using a NICOLET 8700 20 SXC spectrometer (Thermo Fisher). SEM micrographs were taken using a Zeiss DSM 982 Gemini (Carl Zeiss, Jena, Germany) coupled with an Energy dispersive X-ray analyzer (EDX) probe. N₂ adsorption–desorption analysis was performed using an ASAP 2020 system (Micromeritics, USA).

Surface areas were obtained using the Brunauer–Emmett–Teller (BET) method and pore size calculated using the Barrett–Joyner–Halenda (BJH) model.

The flow-through measurements were performed using a peristaltic pump (IPC, Ismatec, Glattbrugg-Zürich, Switzerland), 0.5 mm i.d. PTFE® tubing (Cole Parmer, Chicago, IL, USA), and acrylic minicolumns (MCs) fixed to the PTFE® tubing through 0.25–28 female connectors.

FAAS determinations of cadmium in batch experiments were carried out by running the standard program of the spectrometer Shimadzu AA 6800 (Shimadzu, Kyoto, Japan). A Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory GFA 6000 and an autosampler ASC-6000 was used for the determination of Cd(II) after preconcentration. A cadmium hollow cathode lamp (Hamamatsu Photonics, Japan), deuterium lamp background correction and pyrolytic graphite furnaces were employed throughout the measurements. The temperature programs were those provided by the manufacturer.

2.3. Sample preparation

Tap water from our laboratories and osmosis water samples provided by dialysis treatment centers from Argentina were analyzed without pretreatment.

2.4. Procedures

2.4.1. Synthesis of the mesoporous solids. One-pot synthesis of mesoporous aminopropyl-functionalized silica was performed in a similar manner to that described previously for mercaptopropyl-functionalized silica by Kim *et al.* and Walcarius and Delacôte.^{10,11} The procedure involves the hydrolysis and co-condensation of TEOS and APTES in hydroalcoholic medium using CTAB as a template, and ammonia (28% aqueous) as a catalyst. CTAB (2.4 g) was dissolved in 50 mL of DDW, 45 mL of ethanol (95–96%) and 13 mL of 28% aqueous ammonia. To obtain 20% m/m APTES/TEOS, both components were mixed in appropriate amounts in 5 mL of ethanol as reported elsewhere.^{10,11} The mixture was then added to the “surfactant + catalyst” solution and stirred for 2 h at room temperature.

The obtained solid was filtered and washed several times with DDW and ethanol, and then, it was dried in a vacuum desiccator for 10 h at 100 °C. For the surfactant extraction, the solid was refluxed with 1 mol L⁻¹ HCl in ethanol at 75 °C for 24 h. Finally, it was washed again with ethanol and DDW and dried in the vacuum desiccator for 10 h at 100 °C.

2.4.2. Preparation of HMS-A and HMS-A-PVA composite materials. After three preliminary washings with 1 M HCl and NaOH solutions in order to remove chemical residues (solvents and functionalizing agents) that may be trapped in the resin matrix, the resin was converted into the hydrogen form with 1 M HCl and finally washed with DDW to remove all the excess acid. After drying at 70 °C, the resin was ready for further experimental work.

The HMS-A composite material was prepared by simple mixing of different amounts of the resin with the HMS, leading to composite materials with different proportions of HMS-A.

To prepare the HMS-A-PVA composite, the HMS-A mixture that yielded the best analytical behaviour (details are given below) was impregnated with 1% PVA aqueous solution. Solutions of 1% PVA were prepared by dissolving 1 g of PVA in 100 mL of DDW and then refluxing at 80 °C for 4 h until complete dissolution.

2.4.3. Batch sorption experiments. Batch adsorption experiments were carried out by soaking 25 mg of the different composite materials: HMS, HMS-A (90/10 proportion) and HMS-A-PVA (HMS-A plus 15 µL of PVA 1%), in 10 mL of a Cd solution at room temperature with magnetic stirring. In all cases, suspensions were filtered with a syringe filter of 0.22 µm. Cadmium in the filtered solutions was determined by FAAS. The standard program recommended by the manufacturer was run in all cases.

With the aim of evaluating the influence of pH on the sorption of Cd, HCl, NH₃ or NaOH solutions were employed for pH conditioning (pH 1 to 8). Suspensions were agitated for 24 h, filtered and measured.

For determining the effect of the contact time of the analyte/composite material, the experiments were carried out at the

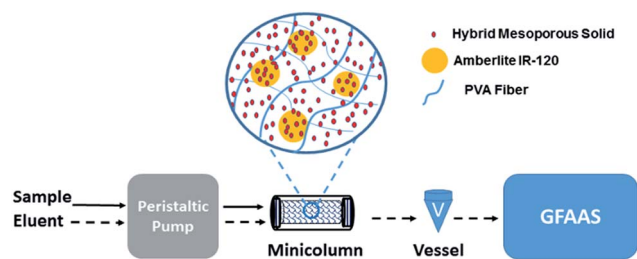


Fig. 1 SPE system. GFAAS: Graphite furnace atomic absorption spectroscopy. Zoomed-in view of the minicolumn filling shows HMS in red circles, Amberlite in yellow circles and PVA fibers in blue strings.

optimum pH, room temperature and definite intervals. The results were modelled with pseudo first order (PO1) and pseudo second order (PO2) models, accordingly to Chiron *et al.*³⁸ For pH sorption and kinetic studies the Cd(II) concentration was 5 mg L⁻¹.

For adsorption isotherms, the experiments were carried out at initial Cd concentrations in the range 5–1000 mg L⁻¹ at the optimum pH. The well-known adsorption isotherm model namely Langmuir was selected to analyze the equilibrium data of cadmium sorption onto the composites.³⁸

The amount of cadmium sorbed (q (mg g⁻¹)) was calculated using the following expression:

$$q_e = \frac{(C_0 - C_e)V}{1000m} \quad (1)$$

where q_e is the sorption capacity in mg g⁻¹, C_0 and C_e are the initial and equilibrium concentrations of Cd in mg L⁻¹, V is the volume of the solution in mL and m is the weight of the sorbent (HMS, HMS-A, and HMS-A-PVA) expressed in g.

2.4.4. Analytical procedure for Cd(II) determinations in minicolumns (MCs). The preconcentration system is shown in Fig. 1. The MC was constructed from an acrylic cylinder (3.0 cm long and 1.6 cm in diameter). The inner part was drilled to obtain inner dimensions equal to 10 mm in length and 0.5 mm i.d. The aspect ratio (length to diameter) was adjusted to ensure minimal dispersion in the system together with lower resistance to the flow stream. The MC was slurry loaded with the solids (0.015 g), one in turn, by means of a syringe and used for over 500 enrichment cycles before repacking. Two plugs of polystyrene foam were placed at both sides of the filler in order to retain the solid.

In a typical experimental procedure under optimized conditions, the sample was introduced into the MC filled with each one or the three composite materials, at a flow rate of 1.0 mL min⁻¹ and a pH value equal to 7.0. The preconcentration time was 10 minutes. 0.5 mL of 0.5 M HCl was employed for elution at a flow rate of 0.5 mL min⁻¹. An aliquot of 50 µL was injected into the graphite furnace, and the analytical signal was thus obtained.

3. Results and discussion

3.1. Characterization

3.1.1. HMS. SEM micrographs of the solid HMS show the morphology of the synthesized material and reveal a sphere-like shape with diameters of 30 ± 3 nm (Fig. 2).

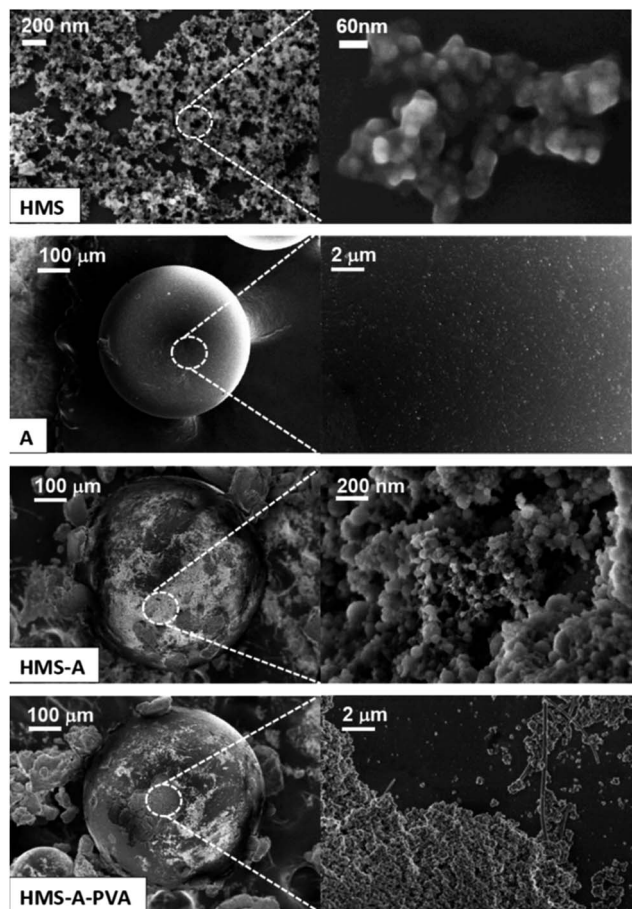


Fig. 2 SEM micrographs of HMS, Amberlite (A), HMS-A and HMS-A-PVA. On the right side: magnification of the micrographs.

The BET measurement shows a surface area of $681 \text{ m}^2 \text{ g}^{-1}$ and a narrow pore size distribution around 3.5 nm, revealing the presence of mesopores in the solid structure.

The FTIR spectrum of the solid HMS (Fig. 3) shows a broad absorption band in the region $3765\text{--}3055 \text{ cm}^{-1}$ attributed to the stretching of the framework Si-OH group with physically adsorbed water molecules. The features around 1084.2 and

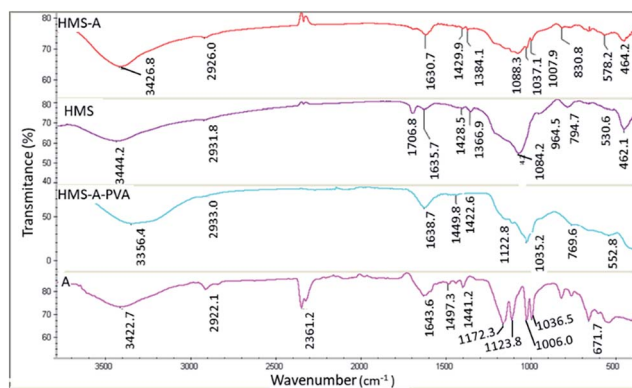


Fig. 3 FTIR spectra of (A): Amberlite, (HMS): hybrid mesoporous solid, (HMS-A): hybrid mesoporous solid 90–10% Amberlite, and (HMS-A-PVA): HMS-A-1% PVA.

964.5 cm^{-1} indicate Si-O-Si and Si-O-H stretching vibrations, respectively. The bands at around 794.7 and 462.1 cm^{-1} result from Si-O vibrations.

The absorption peaks obtained at 1635.7 , 1706.8 and 1418.15 cm^{-1} could be attributed to N-H groups and/or to the ν_{OH} vibration of adsorbed water, while the N-H stretching ($3200\text{--}3500 \text{ cm}^{-1}$) and C-N stretching ($1030\text{--}1230 \text{ cm}^{-1}$) vibrations overlap with the broad absorption band of the silanol group and the Si-O-Si vibrations.^{29,31} On the other hand, the FTIR spectra reveal characteristic peaks from the aliphatic C-H bond and $\text{CH}_2\text{-N}$ bond at 2931.8 cm^{-1} and 1366.9 cm^{-1} , respectively.³¹

Since the evaluation of the template removal was difficult to follow through the IR spectra of the positive counter ion CTA^+ , we studied the elimination of CTAB by the EDX determination of elemental bromine. EDX analysis was performed to test this (see ESI Fig. S1†). Experiments performed on the HMS showed that elemental bromine was completely removed after the HCl/ethanol treatment.

3.1.2. HMS-A and HMS-A-PVA. In order to know more about the interaction between the composite material and the analyte, a study of their composition and morphology was also performed by FTIR and SEM. SEM micrographs reveal that the HMS on the surface of the resin preserves the morphology in both cases: with or without PVA (Fig. 2). As expected, it is also observed that the polymer fibers in the solid HMS-A-PVA cover partially the resin and the HMS.

On the other hand, the FTIR spectra (Fig. 3) reveal the characteristic peaks at around 1400 cm^{-1} for amino groups and vibration bands at around 1100 for the Si-O-Si and 1000 cm^{-1} for the Si-OH groups that are present in HMS-A and HMS-A-PVA.

It is needless to say that the deformation of some of these peaks can be attributed to the overlapping of other major peaks and to the resinsolid interaction (SO_3 symmetric stretching bands at 1006.0 , 1036.5 , 1123.8 and 1172.3 cm^{-1} , SO_2 asymmetric stretching band at 1411.2 cm^{-1} and C=C aromatic nucleus skeletal vibration band at 1643.6 cm^{-1}).³⁹ In the case of HMS-A-PVA, the broader bands assigned to Si-O-Si and Si-OH at 1084.2 and 1005.9 and in the frequency range from 3000 to 3650 cm^{-1} mainly related to hydroxyl groups were correlated to TEOS sol-gel reactions. They could be responsible for the alteration of the three-dimensional structure of the PVA chains.^{35,40}

3.2. Optimization of pH for sorption of Cd(II)

With the aim of modifying the surface charge of the three sorbents, one in turn, and thus, its aptitude for retaining the analyte, changes in the pH of the solutions in contact with the solid were performed in batch (see Fig. 4(a)). The results show that the percentage of extracted cadmium increases with the pH up to a value of 7 where a 99% recovery of the analyte is observed. From $\text{pH} = 7$ onwards no differences were observed. Lower sorption values at pH below 3 were attributed to electrostatic repulsion between cationic cadmium, as $\text{Cd}(\text{H}_2\text{O})_4^{2+}$ and/or CdCl^+ (ref. 41), and the silanols and amino groups, both

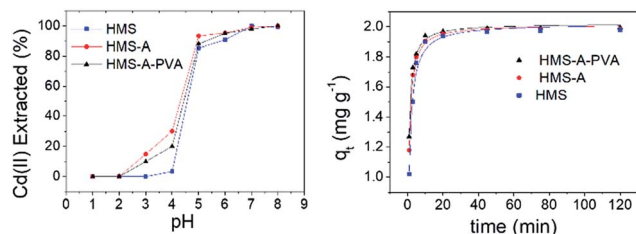


Fig. 4 Effect of pH on the adsorption of Cd(II) (a) and adsorption kinetics (b) for the three sorbents.

protonated.^{29–31} At pH above 5 the efficiency of extraction increases mainly due to a combined effect of adsorption, electrostatic attraction (the surface charge of silica is negative and cadmium speciation is mainly $\text{Cd}(\text{H}_2\text{O})_4^{2+}$) and chelation *via* the deprotonated amino groups. Consequently pH = 7 was selected as the best option for further experiments. Alkaline media were not assayed in order to prevent HMS dissolution or $\text{Cd}(\text{OH})_2$ precipitation.

The three composite materials evidenced the same behaviour with respect to pH. This behaviour is not surprising since the same results are reported in the literature for similar composite materials (PVA-mesoporous silane nanofibers and membranes).^{35,36} Moreover the small amount of resin present in the lab-made sorbents aids this assumption that no changes in pH should be expected.

3.3. Kinetic studies on the adsorption of Cd(II) onto HMS, HMS-A and HMS-A-PVA

Sorption kinetics experiments were performed in order to optimize the design of the flow-through arrangement. The initial sorption velocity studies were of particular relevance due to their influence on the efficiency of SPE at short contact times of the analyte/filler (which is our case). The results show that Cd(II) retention at optimal pH and a Cd(II) concentration of 5 mg g^{-1} increases with time during the first 10 min and then an equilibrium value is reached. It is reasonable to assume that this fast retention equilibrium could be attributed to strong chelation. Experimental data were modelled by means of different kinetic models according to Chiron *et al.*, namely pseudo-first-order and pseudo-second-order.³⁸ Table 1 summarizes the calculated parameters q_e , q_{e_2} , K_1 and K_2 for each one of the composite materials. Pseudo second order (PO2) showed

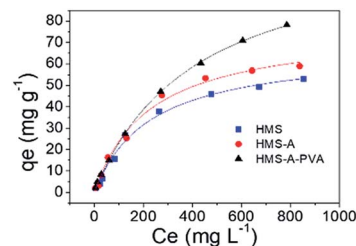


Fig. 5 Adsorption isotherms for Cd(II) onto the three solids: q_e = equilibrium adsorption capacity (mg g^{-1}); C_e = equilibrium concentration (mg L^{-1}).

the best correlation to the experimental data for all the cases (see Fig. 4(b)).

These results suggest that the adsorption of all sorbents could be chemical sorption or chemisorption.³⁵

Experiments performed for both, the bare resin and the bare PVA, showed adsorption for times beyond 60 minutes. Since our experimental conditions consider a contact time for the sample/filling of 10 minutes, the influence of the bare resin and the bare PVA was negligible.

3.4. Cadmium adsorption isotherms

Langmuir isotherm plots for cadmium sorption onto HMS, HMS-A and HMS-A-PVA are shown in Fig. 5. Non-linear regression fittings were employed to calculate the maximum adsorption capacity of Cd ions onto the three sorbents obtaining 67 mg g^{-1} for HMS, 77 mg g^{-1} for HMS-A and 111 mg g^{-1} for HMS-A-PVA. The synergy between the chelating groups could be responsible for the increment of the adsorption capacity of the different sorbents.^{14,35,36}

3.5. Optimization of dynamic conditions for the determination of Cd(II) using minicolumn-GFAAS with the three different sorbents

3.5.1. HMS. Dynamic SPE experiments were assayed in order to reach the best conditions for sorption of the analyte onto the filled MC and its release (see Fig. 1). Since the one variable at a time (OVAT) approach was employed, the mass loading of cadmium was kept constant by passing it through 10 mL of $0.1 \text{ } \mu\text{g L}^{-1}$ Cd(II) at pH = 7 and thus, the best conditions for elution were tested. As mentioned above, Cd(II) is not

Table 1 Kinetic adsorption parameters calculated using pseudo-first-order and pseudo-second-order models for the three filling materials. Concentration of Cd(II) = 5 mg L^{-1} ; Cd(II) volume = 10 mL; sorbent dosage = 0.025 g

Filling composite material	Pseudo-first-order (PO1)			Pseudo-second-order (PO2)		
	$q_{e_1}^a$ (mg g^{-1})	K_1^b (min^{-1})	R^2	$q_{e_2}^c$ (mg g^{-1})	K_2^d ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2
HMS	1.93	0.61	0.93296	2.02	0.52	0.98585
HMS-A	1.93	0.85	0.92253	2.01	0.75	0.99296
HMS-A-PVA	1.94	0.98	0.90568	2.01	0.88	0.99303

^a q_{e_1} = sorption capacity for PO1. ^b K_1 = kinetic constant for PO1. ^c q_{e_2} = sorption capacity for PO2; constant for PO1. ^d K_2 = kinetic constant for PO2.

retained under highly acidic conditions, so it was assumed that a high concentration of acid could be useful for elution. HCl was preferred instead of nitric acid as it prevents oxidation of the amine groups of the filling – enlarging its lifetime – and it is more suitable for GFAAS operation. The effect of HCl concentration on the recovery of Cd(II) was studied from 0.1 to 1 M. Fig. 6(a) shows that from 0.5 M onwards, a quantitative recovery (>98%) of the analyte was observed. Consequently, HCl concentration was fixed at 0.5 M as a compromise between maximum recovery of the analyte and minimal amount of acid inside the graphite furnace. The sample flow rate and eluent flow rate were kept constant at 1 mL min⁻¹ for this preliminary experiment. The effect of the eluent volume on the recovery of Cd(II) was also studied. As shown in Fig. 6(b) the minimum volume of eluent required for quantitative desorption (>98%) was found to be 1.0 mL. After fixing the eluent conditions, the sample and elution volumetric flow rates were optimized one at a time (OVAT). Both variables were changed between 0.5 and 3 mL min⁻¹. As stated above, the selected values need to comply with the following: no filler compaction, no internal pressure increment and maximum preconcentration factor (PCF). Values above 3 mL min⁻¹ were not employed for sample introduction as the solids suffer from compaction with the development of internal pressures and thus, leaking of the flowing solutions. Values below 0.5 mL min⁻¹ were not compatible with the proper operation of the peristaltic pump. It can be seen that a sample flow rate of 1 mL min⁻¹ was the most advantageous for pre-concentration. Lower values produce a low sample throughput and higher values decrease the time of contact between the filling and the analyte and thus, the efficiency of retention. Regarding the eluent flow rate (desorption flow rate), any value below 1 mL min⁻¹ allowed full recovery (>98%). However, an elution flow rate of 0.5 mL min⁻¹ was selected in order to ensure the maximum contact time of the analyte/eluent (Fig. 7).

To summarize, the optimal dynamic conditions using HMS as the sorbent and 10 mL of sample were as follows: sample flow rate 1 mL min⁻¹, 0.5 M HCl at an elution flow rate of 0.5 mL min⁻¹ with an elution volume of 1 mL. Under these conditions, the PCF was 10.

3.5.2. HMS-A and HMS-A-PVA. In order to improve the analytical sensitivity of the proposed methodology, two new composite materials were designed using the HMS synthesized

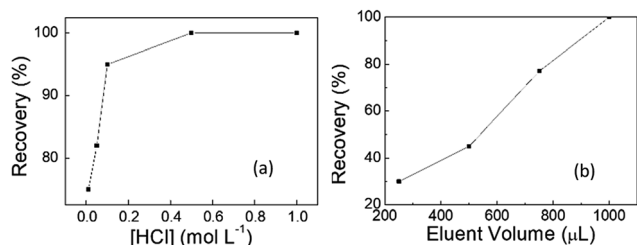


Fig. 6 (a) Percentage recovery for different HCl concentrations. Sample volume: 10 mL of 0.1 ng mL⁻¹ Cd(II), sample flow rate: 1 mL min⁻¹, elution flow rate: 1 mL min⁻¹, eluent volume: 1 mL, PCF: 10. (b) Optimization of elution volume. [HCl]: 0.5 mol L⁻¹, [Cd(II)]: 0.1 ng mL⁻¹, sample volume: 10 mL, adsorption flow rate: 1 mL min⁻¹, desorption flow rate: 0.5 mL min⁻¹.

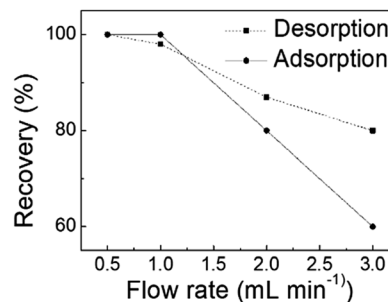


Fig. 7 The effect of sample flow rate on pre-concentration of Cd by passing through 10 mL of 0.1 μg L⁻¹ Cd(II) at pH = 7.

in the laboratory and tested as fillers of the MC. The mass of HMS employed for the three fillers was kept constant as stated above. The first and simpler strategy was to incorporate an exchange resin (Amberlite™ IR120) with the idea of obtaining a greater tortuosity of the pathway within the column, thereby increasing the exposure of the analyte to the amino groups of the solid and/or adding chelating groups provided by the resin. The second design adds to the previous one a polymer with chelating groups at a concentration that ensures adherence but not full coverage. Considering the dimensions of the MC (45 μL bed volume), 10 μL of PVA 1% w/w were chosen as the best option to fulfill these conditions. So, no other amounts of PVA were assayed.

For testing the first design, different blended sorbents were obtained by mixing different quantities of resin and HMS. From here, the solids will be identified as HMS-A, 0–100 indicating the proportion of HMS/resin in each particular case. In order to compare the behaviour of the resin alone and its mixtures with different proportions of the resin, all experiments were performed under the same optimized operational conditions. Taking into account the results for the different proportions of resin (ESI Table S1†) HMS-A 90–10 was chosen as the best option (Cd(II) recovery > 98%).

Studies involving Cd(II) recovery for the optimized proportions of HMS-A and HMS-A-PVA as fillers showed the same performance as that of HMS alone under the conditions described above.

At this point, the reduction of the elution volume becomes the obvious step to test the differences in the behaviour of the solids. To study this, the same experiment was performed by decreasing the elution volume. The results for 750 μL and 500 μL elution volumes showed 97 and 75% Cd(II) recovery respectively for HMS-A filling, and the value was >99% for HMS-A-PVA. In the case of HMS alone, the reduction of the elution volume seriously jeopardizes the analyte recovery which is decreased up to 50% for 500 μL of eluent. These results are in agreement with the hypothesis that, under the optimal dynamic conditions, the exposure of the functional groups of HMS could be the main reason for the greater adsorption in HMS-A. In the case of HMS-A-PVA, the addition of chelating groups provided by hydroxyls could explain the findings.

If the goal is to find the best PCF, the elution volume needs to be reduced and thus, HMS-A-PVA seems to be the best option.

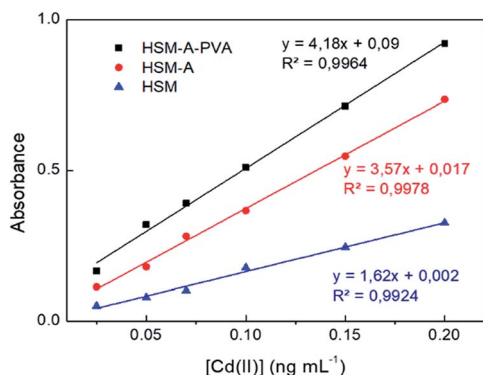


Fig. 8 Working curves for Cd(II) determination. Sample volume: 10 mL, eluent [HCl]: 0.5 mol L⁻¹, eluent volume: 0.5 mL.

3.6. Analytical performance of HMS, HMS-A and HMS-A-PVA MC fillers

For comparison, calibration curves were constructed by concentrating 10 mL of standard solution of Cd (0.02–0.20 ng mL⁻¹) for 10 minutes at a flow rate of 1.0 mL min⁻¹ with an elution volume of 0.5 mL. 50 µL of the eluent were then injected into the furnace. The results of the three different MC fillings employed with the same amount of active solid HMS and under the same experimental conditions are shown in Fig. 8. The fillings are named HMS (only the synthesized solid), HMS-A (solid + resin, 10–90) and HMS-A-PVA (solid + resin and 1% PVA), respectively. Table 2 shows the figures of merit obtained with the three different solids as MC fillers. Note that the three materials could be reused for more than 500 cycles without significant losses in analytical sensitivity (no changes in the

slope of the working curve). Note that the extremely low concentration of cadmium and the short times of contact under dynamic conditions (no need to reach equilibrium) allow this remarkable reuse of the filling. Table 3 shows some figures of merit of the proposed methodology in comparison to other methods recently reported in the literature.^{16–18,30}

Amongst the numerous studies, the references selected are those where the instrumental detection (GFAAS) is not a variable. It can be observed that the dynamic linear range and precision expressed as RSD% are similar. Regarding limits of detection, they are also similar except for ref. 16, which seems rather optimistic considering a limit of quantification (LOQ) equal to 0.01 ng mL⁻¹ (see the reported linear range which is assumed to take its lower value as equal to the LOQ). It is important to note that the analytical method presented here does not require classic or permanent chemical modifiers¹⁵ that usually enlarge the time of operation of the graphite furnace. Moreover, it is suitable for automation which is not the case when strong magnetic fields are employed.¹⁶

It is worth noting that the best performance in terms of number of cycles of sorption/desorption without significant losses of sensitivity is obtained using the procedure presented here. Also a lower sample consumption and higher sample throughput are attained.

3.7. Interference study

Since the ultimate objective of this work is its further application to the determination of Cd(II) in natural waters, the effect of potential ions of usual occurrence in these samples was also carried out. Employing the best performance filling, HMS-A-PVA, in a minicolumn for SPE, different concentrations of

Table 2 Figures of merit for Cd(II) determination: comparison of performance for HMS, HMS-A and HMS-A-PVA

MC filler	LOD ^a (ng mL ⁻¹)	LOQ ^b (ng mL ⁻¹)	RSD% (<i>n</i> = 6; 0.1 ng mL ⁻¹) ^c	%Recovery	Max no. of cycles ^d
HMS-A-PVA	0.0047	0.016	4	100	>600
HMS-A	0.0055	0.018	6	85	500–600
HMS	0.0121	0.040	11	39	500

^a LOD is defined as 3S_b/m. ^b LOQ is defined as 10S_b/m, respectively, where S_b is the SD of ten measurements of a procedural blank and *m* is the slope of the calibration graph. ^c Obtained with solid synthesized on different days. ^d Max no. of cycles: maximum number of cycles. Cycle: sorption/desorption under optimal conditions. [Cd(II)]: 0.1 ng mL⁻¹, sample volume: 10 mL, eluent [HCl]: 0.5 mol L⁻¹, eluent volume: 0.5 mL, maximum PCF under optimal conditions: 20.

Table 3 Comparison of the analytical performance of the presented method with recently reported nanomaterial-based methods for pre-concentration of cadmium

Method	Sorbent	V _s ^e (mL)	ST ^f (h ⁻¹)	LOD (ng mL ⁻¹)	Linear range (ng mL ⁻¹)	RSD (%)	Max no. cycles	Reference
MSPE ^a -GFAAS	MMCN ^b	10	4	0.0012	0.01–10	2.3	100	16
MSPE ^a -GFAAS	II-MMS ^c	25	2	0.0061	0.01–0.20	4	8	30
SPE-GFAAS	NH2-IL/SG	50	3	0.0089	0.05–0.20	2.3	53	17
MSPE ^a -GFAAS	MAC ^d	100	10	0.0040	0.01–0.70	3.5	5	18
SPE-GFAAS	HMS-A-PVA	10	5	0.0047	0.02–0.20	4	>600	This work

^a Magnetic solid phase extraction. ^b Magnetic multiwalled carbon nanotubes. ^c Cd(II)-ion imprinted magnetic mesoporous material. IL/SG: ionic liquid/silica gel. ^d Magnetic activated carbon nanocomposite. ^e V_s = sample volume. ^f ST = sample throughput.

Table 4 Maximum tolerable concentration (MTC) of interferents in the determination of Cd(II) under optimized conditions. FPC: 20, [Cd(II)] = 0.1 ng mL⁻¹

Interferent	MTC (ng mL ⁻¹)	Recovery (%)
Pb(II)	100	99 ± 1
Zn(II)	75	100 ± 1
Ni(II)	50	99 ± 2
Co(II)	50	97 ± 2
Na(I)	20 000	100 ± 1
Cl ⁻	50 000	98 ± 2
NO ₃ ⁻	50 000	99 ± 2

Table 5 Analysis of Cd(II) ions in different real samples (mean ± SD, n = 3)

Sample	C _{added} (ng L ⁻¹)	C _{found} (ng L ⁻¹)	Recovery%
Osmosis water	0	N.D.	—
	50	49.7 ± 3.2	99.3
	100	100.5 ± 2.0	100.5
Tap water	0	N.D.	—
	50	50.2 ± 2.5	100.3
	100	103.3 ± 3.0	103.3

Pb(II), Ni(II), Co(II), Zn(II), Na(I), chloride and nitrate ions, one in turn, were added to Cd(II) solutions. It was shown that no interference of the analytical signal was observed for concentrations up to 10 times higher than those typically present in river waters, which makes this approach suitable to perform the determination in such kind of samples (Table 4).

3.8. Applications to real samples

The suitability for the analysis of real samples with the HMS-A-PVA filler under optimal conditions was investigated through Cd determination in osmosis and tap water, as shown in Table 5. As the Cd concentration in the analysed samples was below the detection limit achieved here (see Table 3), traces of Cd of known amounts were spiked into the samples and recovery values ranging between 99 and 103% were obtained.

4. Conclusions

This work shows an easy way to improve the analytical performance of cadmium determination *via* a rational design of composite materials for preconcentration purposes that combines the complexing ability of the different components of the filling together with the dynamic conditions imposed by a flow-through system holding a packed minicolumn. Overpressure was prevented together with bleeding of the solid. As described above, HMS-A-PVA proved to be the best option for these purposes. Moreover, the proposed methodology does not require toxic organic solvents and shows slow sample consumption, high sample throughput, a similar LOD to methods already reported and excellent reusability. It was applied to real water samples with good percentages of recovery after the addition of ultratrace amounts of cadmium.

Conflicts of interest

The authors declare no conflicts of interest concerning this article.

Acknowledgements

The authors gratefully acknowledge financial support from the following agencies and organisations: Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET, Argentina (grant number 11220130100140CO) and UBACyT, Ciencia y Técnica de la Universidad de Buenos Aires (grant number 20020130100099BA).

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